Notes

A Method for Determining the 1-Octanol/Water Partition Coefficients of Volatile Hydrocarbons

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It is a common practice to use the 1-octanol/water partition coefficient (K_{ow}) as a measure of lipophilicity.[1] Organic compounds with large K_{ow} values are liable to bioconcentrate in living tissue and to adsorb on soil.[2] The solubilities of various hydrocarbons in water have also been correlated to their K_{ow} values.[3]

There are several techniques to determine K_{ow}: a generator-column[4], reversed-phase HPLC[5], centrifugal partition chromatography[6], and a shake-flask. Of these, although the last one is classic, it is still the most popular and widely applicable method. The shake-flask method is literally based on shaking a solute with two immiscible solvents, 1-octanol and water, in a flask. Once the partition equilibrium is attained, the solute concentration in one or both phases is measured. The main disadvantage of this shake-flask method is the formation of emulsions during shaking, which affects the observed K_{ow} values; the aqueous phase often needs to be centrifuged to remove most of the small 1-octanol droplets. In order to avoid this problem, a "slow-stirring method" has recently been proposed.[7]

Stable and hydrophobic nonelectrolytes are generally more or less volatile. The new method proposed here is applicable to such solutes. This method is based essentially on the same principle as the shake-flask method, but the 1-octanol phase is not allowed to contact directly with water. Instead, air is bubbled through the 1-octanol phase, in which the solute of interest has been dissolved, so as to produce a solute vapor. The vapor is introduced into a separate water phase and circulated in a closed system. The partition equilibrium of the solute between the 1-octanol and water phases can be attained within a relatively short time; 1-octanol droplets are not observed in the water phase.

Experimental

Reagents

All of the reagents were of analytical reagent grade and used as received. Deionized distilled water was used throughout the experiments. Each hydrocarbon was dissolved in water-saturated 1-octanol to prepare the sample solution: 0.0100 M (1 M≡1 mol/dm^3) for biphenyl, naphthalene, phenanthrene, and 1,4-dichlorobenzene, 0.0500 M for pyrene, and 0.100 M for the other hydrocarbons.

Apparatus and procedure

The device used to equilibrate volatile hydrocarbons between 1-octanol and water was essentially the same as that mentioned in a previous paper;[8] polytetrafluoroethylene (PTFE) film and a trap were removed from the device for the present use. The device consisted of three parts: a cylindrical separatory funnel (6.5 cm i.d., 600 cm^3 capacity), a test-tube (2.8 cm i.d.×25 cm), and a Viton diaphragm airpump (Iwaki Co., AP-032Z). The three parts were connected with PTFE tubings to make a closed system. To the funnel and the test-tube were attached jackets, through which water was made to flow so as to maintain the temperature of each content at 25.0±0.1°C. The device was placed in a room where the temperature was held at a temperature higher than 25°C.

Water, which had been saturated with 1-octanol, was placed up to 400 cm^3 in the funnel, and a 20 cm^3 portion of the 1-octanol sample solution was added to the test-tube. Using the pump, air was bubbled through the sample solution *via* a glass capillary. The resulting solute (and 1-octanol) vapor was dispersed in water *via* a glass capillary and circulated in the closed system. The flow rate of the airpump was set at 100 to 500 cm^3/min by regulating the voltage applied to the pump.

After a prescribed vapor-circulation period, a 50 to 300 cm^3 portion of the aqueous phase, depending on the concentration of the solute in the aqueous phase and on the detector sensitivity, was withdrawn to an extraction funnel, in which a 5 cm^3 portion of cyclohexane had been placed in advance. The cyclohexane extract was analyzed with a Hitachi (Model 100-50) spectrophotometer at an appropriate wavelength for each hydro-

carbon. Calibration graphs were prepared for each hydrocarbon by shaking the same volume of water as that used in practice with 5 cm^3 cyclohexane solutions of a hydrocarbon of known concentration. The concentration of the hydrocarbon in the 1-octanol phase was not measured in this work; it was shown by preliminary runs that the hydrocarbon concentration in the 1-octanol sample solution did not change appreciably after vapor-circulation runs. The 1-octanol/water partition coefficient is defined as the ratio of the molar concentration of solute in 1-octanol saturated with water to its concentration in water saturated with 1-octanol, under equilibrium conditions.

Results and Discussion

Nine hydrocarbons were used as solutes in this work. The concentrations of the solutes in the aqueous phase are shown in Fig. 1 as a function of the vapor-circulation time; the time to attain a constant value depended on the solute used. It took at longest 4 h in the case of pyrene.

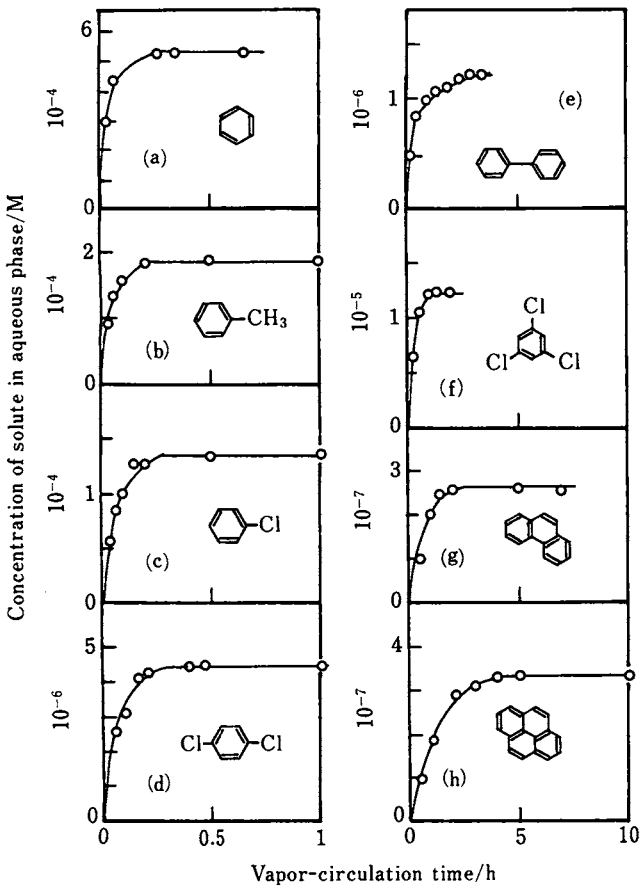

Fig. 1 Concentration of the solute in the aqueous phase *vs.* the vapor-circulation time. Organic phase, 1-octanol. Solute: benzene (a), toluene (b), chlorobenzene (c), 1,4-dichlorobenzene (d), biphenyl (e), 1,3,5-trichlorobenzene (f), phenanthrene (g), and pyrene (h).

The conventional shake-flask method may reduce the time to attain the partition equilibrium of a solute between aqueous and octanol phases when the two phases are vigorously shaken. Particular attention, however, should be paid during the shake-flask so as not to produce any emulsions.

Miller *et al.* have prepared aqueous solutions in equilibrium with 1-octanol containing a solute by gentle stirring for at least 24 h with a PTFE-coated magnetic stirrer without breaking up the 1-octanol/water interface or by gentle shaking for 24 h and then leaving it to settle for at least 48 h before making an analysis.[3] They reported that no emulsion formation was observed in the aqueous phase. However, the formation of emulsions was suggested by Bruijn *et al.*[7], who proposed the slow-stirring method. The basis for this suggestion is that the equilibrium concentration of 1-octanol is considerably lower in water prepared by the slow-stirring method than in water prepared by the method of Miller *et al.* The slow-stirring method requires one to several days to reach partition equilibrium.

The 1-octanol/water partition coefficients determined in this work are given in Table 1 together with literature values taken from two groups. Our data are in reasonable agreement with the literature values. Taking biphenyl as a test solute, we measured the concentration of this solute both in water and in water saturated in advance with 1-octanol. The difference was found to be negligible. This observation agrees with the experimental results of Miller *et al.*[3]

In an attempt to demonstrate that the present vapor-circulation method is also applicable to organic solvents other than 1-octanol, the partition coefficients of naphthalene and chlorobenzene between water and normal alcohols of C_4 to C_7 have been determined. These alcohols were saturated with water; water was saturated in advance with an alcohol of interest. The concentrations of naphthalene in the aqueous phase are shown in Fig. 2 as a function of the vapor-circulation time. A constant concentration of naphthalene in the aqueous phase, which increases as the number of carbon of alcohol decreases, is reached after 1 h for C_8 to C_5 alcohols, while it takes 6 h for 1-butanol. The partition coefficients of naphthalene and chlorobenzene calculated

Table 1 Logarithms of 1-octanol/water partition coefficients of selected solutes at 25°C

Solute	This work	Ref. 3	Ref. 7
Benzene	2.26±0.01	2.13	2.186±0.009
Toluene	2.73±0.01	2.65	2.786±0.005
Chlorobenzene	2.88±0.01	2.98	2.898±0.004
1,4-Dichlorobenzene	3.35±0.01	3.38	3.444±0.030
Naphthalene	3.40±0.01	3.35	
Biphenyl	3.95±0.02	3.95	4.008±0.022
1,3,5-Trichlorobenzene	3.91±0.01	4.02	4.189±0.019
Phenanthrene	4.57±0.02	4.57	4.562±0.006
Pyrene	5.17±0.01	5.18	

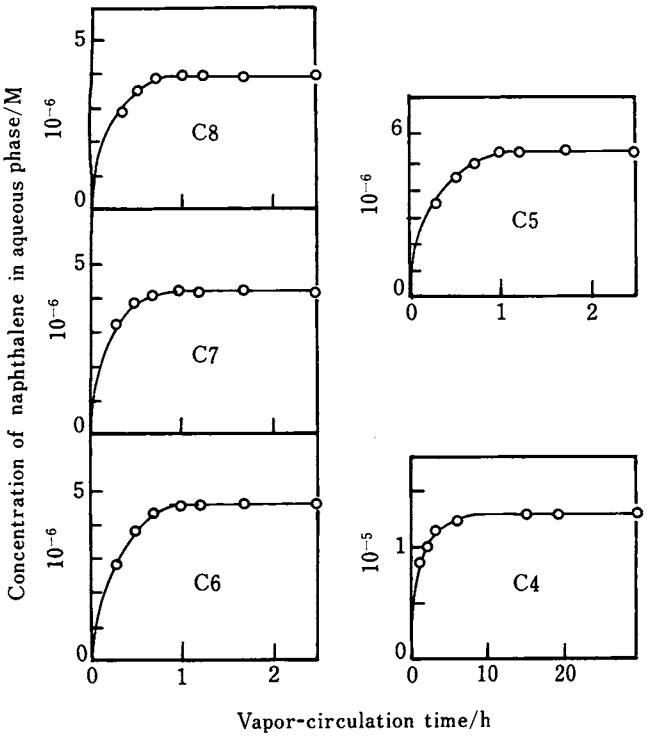

Fig. 2 Concentration of naphthalene in the aqueous phase *vs.* the vapor-circulation time. Organic phase: 1-octanol (C_8), 1-heptanol (C_7), 1-hexanol (C_6), 1-pentanol (C_5), and 1-butanol (C_4).

Table 2 Logarithms of alcohol/water partition coefficients of naphthalene and chlorobenzene at 25°C

Alcohol	Partition coefficient	
	Naphthalene	Chlorobenzene
1-Heptanol	3.38±0.01	2.83±0.01
1-Hexanol	3.34±0.01	2.82±0.01
1-Pentanol	3.26±0.01	2.78±0.01
1-Butanol	2.89±0.01	2.75±0.02

for C_7 – C_4/water systems are given in Table 2. It is reasonable, in view of the hydrophobicity of the alcohol, to expect that naphthalene and chlorobenzene should have stronger affinities for alcohols with a longer alkyl chain.

Although the vapor-circulation method proposed here is only applicable to volatile solutes, it has two advantages over the conventional shake-flask method. First, partition equilibrium can be attained in a relatively short time without any formation of emulsions of the organic phase. Second, the present method is potentially applicable to such cases in which the partition coefficient of a volatile solute is needed in the aqueous phase where other solutes, which are non-volatile, but yet more or less hydrophobic in nature, such as surfactants, are present. The shake-flask method (and also the generator-column, HPLC, and centrifugal partition chromatographic methods) cannot be applied to such systems, because non-volatile solute molecules coexisting in the aqueous phase are more or less soluble in 1-octanol (or more generally, in organic solvents) while shaking or being in contact with water. If, therefore, one needs some information about a coexisting solute, such as its solubilization effect on a volatile solute, by measuring partition of the volatile solute, the organic phase should not be allowed to directly contact the aqueous phase.

A headspace gas chromatographic method has recently been proposed to measure the partition coefficients of volatile solutes.[9] The present method is comparable to this method regarding the two points mentioned above. Although the latter method requires no standard solution of the solute, the solute should be sufficiently volatile to be measured using a chromatographic detector.

References

1. S. H. Yalkowsky and S. Banerjee, "*Aqueous Solubility, Methods of Estimation for Organic Compounds*", Marcel Dekker, New York, 1992.
2. A. Opperhuizen, P. Serné and J. M. D. Van der Steen, *Environ. Sci. Technol.*, **22**, 286 (1988).
3. M. M. Miller, S. P. Wasik, G.-L. Huang, W.-Y. Shiu and D. Mackay, *Environ. Sci. Technol.*, **19**, 522 (1985).
4. Y. B. Tewari, M. M. Miller, S. P. Wasik and D. Martire, *J. Chem. Eng. Data*, **27**, 451 (1982).
5. B. McDuffie, *Chemosphere*, **10**, 73 (1981).
6. R. A. Menges, G. L. Bertrand and D. W. Armstrong, *J. Liq. Chromatogr.*, **13**, 3061 (1990).
7. J. D. Bruijn, F. Busser, W. Seinen and J. Hermens, *Environ. Toxicol. Chem.*, **8**, 499 (1989).
8. I. Sanemasa, T. Tochihara and T. Deguchi, *Bunseki Kagaku*, **39**, 239 (1990).
9. J. Li and P. W. Carr, *Anal. Chem.*, **65**, 1443 (1993)

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